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(54) Title: CLEAR, THICKENED TOPICAL SKIN CARE COMPOSITION WITH WATER-INSOLUBLE PERFUME

(57) Abstract

Provided are clear, perfume-containing, thickened aqueous compositions comprising: (a) an aqueous hydrogel comprising from about 0.1 % to about 10 %, by weight, hydrogel forming polymeric gelling agent, calculated on dry polymeric gelling agent weight basis; (b) from about 0.1 % to about 15 %, by weight, nonionic surfactant; (c) from about 0.05 % to about 5 %, by weight, water-insoluble perfume; and (d) from about 50 % to about 99.75 %, by weight, water; wherein said composition has a viscosity at 25 °C of at least about 4,000 centipoise; and contains a sufficient amount of said nonionic surfactant to provide said perfume in solubilized form, whereby said composition is clear.

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**CLEAR, THICKENED TOPICAL SKIN CARE COMPOSITION  
WITH WATER-INSOLUBLE PERFUME**

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**FIELD OF INVENTION**

This invention relates to topical skin care compositions. More particularly, this invention relates to thickened, fragrant topical skin care compositions which are clear.

**BACKGROUND OF THE INVENTION**

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A wide variety of skin care compositions are topically applied to achieve cosmetic and/or medical benefits. Exemplary types of such compositions include skin conditioning compositions, sunscreen compositions, fragrances and colognes, after-shave compositions, and skin renewal compositions. In many of these compositions, it is desirable for the composition to have a pleasing or otherwise identifiable fragrant scent which can be smelled by the persons using or applying the composition. In other cases, it is desirable to use an odor masking compound instead of or in addition to the other fragrance components. In many of these compositions, such as after-shaves, perfume compositions, and colognes, a pleasing or unique scent can, in fact, be an important purchasing criteria for users of the product. Many of the perfumes commonly used to create desirable scents and odor masking qualities will contain water-insoluble compounds.

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It can also be desirable for these products to be thickened, such as in the form of a gel, so that the product is less thin and runny, is easy to apply to the skin, is suitable for suspending other active ingredients (e.g. skin conditioners, or is of comparable product viscosity to other conventional products of the same type. Additional benefits may include improved skin feel and stability of other components in the product. A wide variety of thickeners have been used in the area of topical skin care compositions. These include, for example, hydroxylated vinylic polymers, homopolymers of acrylic acid crosslinked with an alkyl ether of pentaerythritol or an allyl ether of sucrose, carboxymethylcelluloses such

as hydroxypropyl methylcellulose, microcrystalline cellulose, aluminum silicates and magnesium aluminum silicates, ethylene glycol di- and mono- stearates, etc. Of these, it is particularly common to use acrylic and crosslinked polymers in the area of fragrant skin care compositions.

- 5 These polymers as are typically found in skin care products are referred to in the art as "carbomer" polymers, according to the Cosmetic, Toiletries, and Cosmetics Association (CTFA).

It is also desirable to provide clear, thickened compositions for application to the skin which contains perfume. It is especially desirable to formulate such a composition that is thickened with an acrylic acid crosslinked polymer since they provide highly desirable properties as vehicles for thickened topical skin care formulations. In particular, for example, they form gels which rapidly breakdown upon contact with skin surface electrolytes, thereby transforming from a gel to an easily spreadable liquid, for aesthetically pleasing and even distribution across the skin surface. However it has been found to be difficult to form clear aqueous solutions containing both water-insoluble perfume oils and carbomer-type thickeners, even in the presence of emulsifiers.

It is therefore an object of this invention to provide a clear, fragrant, thickened topical skin care compositions. In particular, it is an object of this invention to provide such a composition which contains both water-insoluble perfume oils and a thickening agent while still being clear.

It is another object of this invention to provide a process for making topical skin care compositions meeting the above objects.

These and other benefits as may be discussed herein or apparent to one skilled in the art can be provided according to the invention which is described below.

All percentages herein are by weight of the composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

The invention hereof can comprise, consist of, or consist essentially of the essential elements described herein as well as any of the preferred or optional ingredients also described herein. Nothing

herein is meant to be interpreted to exclude the use or presence of other components or steps except as may be otherwise indicated.

#### SUMMARY OF THE INVENTION

The present invention provides a clear, water insoluble perfume-  
5 containing, thickened, aqueous composition suitable for topical  
application to the skin. The present compositions comprise water-  
insoluble perfume, water, a sufficient amount of nonionic emulsifier to  
solubilize the perfume in the composition, and a hydrogel forming  
polymeric gelling agent. The particular viscosity of the compositions of  
10 the present invention is not critical, although for purposes hereof the  
compositions should be sufficiently thickened such that they have a  
viscosity of at least about 4,000 centipoise at 25°C.

More specifically, the compositions of the present invention can be  
described as clear, perfume-containing, thickened aqueous compositions  
15 comprising:

- (a) an aqueous hydrogel comprising from about 0.1% to about 10%,  
by weight, hydrogel forming polymeric gelling agent, calculated on  
dry polymeric gelling agent weight basis;
- (b) from about 0.1% to about 15%, by weight, nonionic surfactant;
- 20 (c) from about 0.05% to about 5%, by weight, water-insoluble  
perfume; and
- (d) from about 50% to about 99.75%, by weight, water;

wherein said composition has: a viscosity at 25°C of at least about 4,000  
centipoise; and contains a sufficient amount of said nonionic surfactant to  
25 provide said perfume in solubilized form, whereby said composition is  
clear.

The present invention, as well as various optional and preferred  
embodiments thereof, are described in more detail below.

#### DETAILED DESCRIPTION OF THE INVENTION

##### 30 Hydrogel Forming Polymeric Gelling Agent

The compositions will comprise aqueous gel formed from a highly  
absorbent hydrogel forming polymeric gelling agent. The compositions  
will contain from about 0.1% to about 10%, by weight of the composition,  
preferably from about 0.2% to about 5%, more preferably from about  
35 0.3% to about 1%, of such hydrogel forming polymeric gelling agent,  
calculated based on the dry weight of the hydrogel forming polymeric  
gelling agent.

The hydrogel forming polymeric gelling agent hereof is highly absorbent of water, and will generally be able to absorb at least about 40 g deionized water per gram of gelling agent, preferably at least about 60 g/g, more preferably at least about 80 g/g. The absorbing capacity can be determined as described below.

Cut Dexter #1234T heat sealable tea bag stock or equivalent into 6 cm x 12 cm strips, fold lengthwise across the short axis and heat seal two of the three open sides so that the inside edges of the seals are about 3.0 to 5.0 mm from the edge of the tea bag. Place about 0.200 g (dry weight, ambient conditions; "W<sub>NET</sub>") of hydrogel forming polymeric gelling agent into the tea bag and heat seal the remaining unsealed edge. Prepare a blank (empty tea bag) for each sample. The polymeric gelling agent should be well mixed immediately prior to preparing each of the tea bags. Hold each tea bag containing the polymeric gelling agent horizontally and evenly distribute the polymeric gelling agent throughout the bag. Lay each tea bag (including the blank) horizontally in a container containing deionized water of 2.5 cm in depth and hold at the top surface of the water for one minute, allowing the entire surface of the tea bag to wet out. Submerge each tea bag for 20 minutes, remove it, and hang dry for five minutes. Weigh each wet tea bag and record weights in grams for the wet sample tea bag (W<sub>w</sub>) and the wet blanks (W<sub>b</sub>). Calculate Absorbent Capacity as follows:

$$\text{Absorbent Capacity (g/g)} = \frac{W_w - (W_b + W_{\text{NET}})}{W_{\text{NET}}}$$

The hydrogel of the present composition must contain a sufficient level of absorbed water such that the composition is clear and the hydrogel forming polymeric gelling agent itself appears only as a clear gel, rather than as non-clear particulate matter. "Clear" for purposes of the present invention, means a clarity of about 20 Nephelometric Turbidity Units (NTU) or less, preferably about 17 NTU or less, more preferably about 15 NTU or less, at 25°C. In general the turbidity for most formulations hereof will be about 5 NTU (at 25°C) or more, more generally about 10 NTU or more, although lower NTU levels are not intended to be excluded. Clarity is measured using a photoelectric turbidimeter which measures a nephelometric signal (90° scatter turbidimeter), such as a Hach Ratio/XR Turbidimeter (Hach Company,

Loveland, Colorado, USA), or Orbeco-Hellige turbidimeter (Orbeco Analytical Systems, Inc., Farmingdale, NY, USA) or equivalent, calibrated to the formazin standard. The formazin standard is well known in the art and is also forth by the American Public Health Association (APHA) in Standard Methods For The Examination of Water and Wastewater, 18th edition, 1992, Chapter 2, pp 8-11.

The hydrogel forming polymeric material, when in dry form prior to incorporation into the compositions will generally be in the form of particles or fibers. Particles will preferably have a weight average particle size (diameter, or equivalent diameter in the case of non-spherical particles) of from about 5 to about 500 microns, preferably from about 10 to about 60 microns, more preferably from about 10 to about 50 microns. Fibrous hydrogel forming polymeric gelling agent preferably have diameters (or equivalent diameters in the case of non-round fibers) of from about 5 to about 100 microns, preferably from about 15 to about 50 microns, and lengths of from about 0.1 mm to about 5 mm more preferably from about 0.5 mm to about 2 mm. It is contemplated that larger or smaller particles or fibers can be used, although they are not preferred, as larger particles or fibers may provide a grainier or a more string-like product feel, and smaller particles may result in processing difficulties. If relatively large particles or fibers are used during manufacture, improved finished product aesthetics can be obtained by sheer mixing the compositions or other mixing operations during processing of the compositions.

In general, the hydrogel forming polymeric gelling agent materials of the present invention are at least partially crosslinked polymers prepared from polymerizable, unsaturated acid-containing monomers which are water-soluble or become water-soluble upon hydrolysis. These include monoethylenically unsaturated compounds having at least one hydrophilic radical, including olefinically unsaturated acids and anhydrides which contain at least one carbon-carbon olefinic double bond.

With respect to these monomers, water-soluble means that the monomer is soluble in deionized water at 25°C at a level of at least 0.2%, preferably at least 1.0%.

Upon polymerization, monomeric units as described above will constitute from about 50 mole percent to 99.999 mole percent, more preferably from about 75 mole percent to 99.99 mole percent of the

polymeric gelling agent material (dry polymer weight basis). Two or more different monomer types of the previously described acid group-containing monomers may be copolymerized in order to provide the hydrogel-forming polymeric gelling material. Exemplary types of such acid groups and other hydrophilic groups include carboxyl, carboxylic acid anhydride, carboxylic salt, sulfonic acid, sulfonic acid salt, hydroxyl, ether, amide, amino and ammonium salt groups.

Hydrogel forming polymeric gelling agents suitable for use herein are well known in the art, and are described, for example, in U.S. Patent 4,076,663, Masuda et al., issued February 28, 1978; U.S. Patent 4,062,817, Westerman, issued December 13, 1977; U.S. Patent 4,286,082, Tsubakimoto et al., issued August 25, 1981; U.S. Patent 5,061,259, Goldman et al., issued October 29, 1991, and U.S. Patent 4,654,039, Brandt et al., issued March 31, 1987 and the U.S. Reissue Patent thereof, RE 34,649, issued April 19, 1988, all of which are incorporated herein in their entirety.

Fibrous hydrogel forming polymeric gelling agents are described in U.S. Patent 4,731,067, Le-Khac, issued March 15, 1988, U.S. Patent 4,743,244, Le-Khac, issued May 10, 1988, U.S. Patent 4,813,945, Le-Khac, issued March 21, 1989, U.S. Patent 4,880,868, Le-Khac, issued November 14, 1989, U.S. Patent 4,892,533, Le-Khac, issued January 9, 1990, U.S. Patent 5,026,784, Le-Khac, issued June 25, 1991, U.S. Patent 5,079,306, Le-Khac, issued January 7, 1992, U.S. Patent 5,151,465, Le-Khac, issued September 29, 1992, U.S. Patent 4,861,539, Allen, Farrer, and Flesher, issued August 29, 1989, and U.S. Patent 4,962,172, Allen, Farrer, and Flesher, issued October 9, 1990, all incorporated herein by reference in their entireties.

Examples of suitable water-soluble monomers are as follows:

1. Carboxyl group-containing monomers (carboxylic acid-containing): monoethylenically unsaturated mono or poly-carboxylic acids, such as (meth) acrylic acid (meaning acrylic acid or methacrylic acid. Similar notations are used hereinafter), maleic acid fumaric acid, sorbic acid, itaconic acid, citraconic acid, tricarboxy ethylene, and ethacrylic acid;
2. Carboxylic acid anhydride group-containing monomers: monoethylenically unsaturated polycarboxylic acid anhydrides, such as maleic anhydride;



3. Carboxylic acid salt-containing monomers: water-soluble salts (alkali metal salts, ammonium salts, amine salts, etc.) of monoethylenically unsaturated mono- or poly- carboxylic acids [such as sodium (meth)acrylate, trimethylamine (meth)acrylate, triethanolamine (meth) acrylate, sodium maleate, methylamine maleate];

4. Sulfonic acid group-containing monomers: aliphatic or aromatic vinyl sulfonic acids (such as vinylsulfonic acid, allyl sulfonic acid, vinyltoluenesulfonic acid, styrene sulfonic acid), (meth)acrylic sulfonic acids [such as sulfopropyl (meth) acrylate, 2-hydroxy-3-(meth)acryloxy propyl sulfonic acid, 2-acylamido-2-methyl propane sulfonic acid];

5. Sulfonic acid salt group-containing monomers: alkali metal salts, ammonium salts, amine salts of sulfonic acid group-containing monomers as mentioned above.

6. Hydroxyl group-containing monomers: monoethylenically unsaturated alcohols [such as (meth)allyl alcohol], monoethylenically unsaturated ethers or esters of polyols (alkylene glycols, glycerol, polyoxyalkylene polyols), such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, triethylene glycol (meth)acrylate, poly(oxyethylene oxypropylene) glycol mono (meth)allyl ether (in which hydroxyl groups may be etherified or esterified).

7. Amide group-containing monomers: (meth) acrylamide, N-alkyl (meth)acrylamides (such as N-methylacrylamide, N-hexylacrylamide), N,N-dialkyl (meth)acryl amides (such as N,N-dimethylacrylamide, N,N'-di-n-propylacrylamide), N-hydroxyalkyl (meth)acrylamides [such as N-methylol(meth)acrylamide, N-hydroxyethyl (meth)acrylamide], N,N-dihydroxyalkyl (meth)acrylamides [such as N,N-dihydroxyethyl (meth)acrylamide], vinyl lactams (such as N-vinylpyrrolidone);

8. Amino group-containing monomers: amino group-containing esters (e.g. dialkylaminoalkyl esters, dihydroxyalkylaminoalkyl esters, morpholinoalkyl esters, etc.) of monoethylenically unsaturated mono- or di-carboxylic acid [such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, morpholinoethyl (meth)acrylate, dimethyl aminoethyl fumarate], heterocyclic vinyl compounds [such as vinyl pyridines (e.g. 2-vinyl pyridine, 4-vinyl pyridine, N-vinyl pyridine), N-vinyl imidazol]; and

9. Quaternary ammonium salt group-containing monomers: N,N,N-trialkyl-N-(meth)acryloyloxyalkylammonium salts [such as N,N,N-trimethyl-N-(meth)acryloyloxyethylammonium chloride, N,N,N-triethyl-N-

(meth)acryloyloxyethylammonium chloride, 2-hydroxy-3-(meth)acryloyloxypropyl trimethyl ammonium chloride], and monomers as mentioned in British patent specification No. 1,034,296.

5        Suitable monomers which become water-soluble by hydrolysis, for use in this invention instead of or in conjunction with the water-soluble monomers, include monethylenically unsaturated compounds having at least one hydrolyzable group, such as ester and nitrile groups. Such monomers having an ester group include for example, lower alkyl (C1-C3) esters of monoethylenically unsaturated carboxylic acids, such as  
10        methyl (meth)acrylate, ethyl (meth)acrylate and 2-ethylhexyl (meth)acrylate; and esters of monoethylenically unsaturated alcohols [vinyl esters, (meth)-allyl ester, etc.], such as vinyl acetate and (meth) allyl acetate. Suitable nitrile group-containing monomers include (meth) acrylonitrile.

15        Preferred monomers include carboxylic acid monomers, or anhydrides or salts thereof. Especially preferred monomers include acrylic acid and methacrylic acid and anhydrides and salts thereof. Acrylic acid itself is most preferred for preparation of the polymeric gelling agent material.

20        While at least 50 mole percent of the hydrogel-forming polymer compositions herein should be prepared from acid group-containing monomers, some non-acid monomers may also be used to prepare the hydrogel-forming polymer compositions herein (prior to neutralization). Such non-acid monomers can include, for example, the water-soluble or  
25        water-dispersible esters of the foregoing acid-containing monomers as well as monomers which contain no carboxyl or sulfonic acid groups at all. Optional non-acid monomers can thus include, for example, carboxylic acid or sulfonic acid ester-containing monomers, hydroxyl group-containing monomers, amide group-containing monomers, amino  
30        group-containing monomers, nitrile group containing monomers and quaternary ammonium salt group-containing monomers. These non-acid monomers are well known materials and are described in greater detail, for example, in Masuda et al., U.S. Patent 4,076,663, issued February 28, 1978; and in Westerman, U.S. Patent 4,062,817, issued December  
35        13, 1977; both of which are already incorporated herein by reference. If present at all, such non-acid monomers should generally be used only to such an extent that, prior to neutralization, no more than about 50% mole

percent of the polymer compositions herein are prepared from such non-acid monomers.

In the hydrogel-forming polymeric gelling agent the polymeric component formed from unsaturated, acid-containing monomers may be grafted on to other types of polymer moieties such as starch or cellulose.

Suitable starches include, for example, natural starches such as sweet potato starch, potato starch, wheat starch, corn starch, rice starch, tapioca starch, and the like, and processed or modified starches such as alpha-starch, dextrine, oxidized starch, dialdehyde starch, alkyl-etherified starch, allyl-etherified starch, oxyalkylated starch, aminoethyl-etherified starch, cyanoethyl-etherified starch and the like.

Suitable celluloses include, for example, celluloses obtained from wood, leaves, stems, bast, seed fluffs, and the like; and modified celluloses such as alkyl-etherified cellulose, organic-acid-esterified cellulose, oxidized cellulose, hydrocellulose, and the like. Starch grafted materials of this type are especially preferred for use herein.

In general, the molecular weight (mass average) of the base polymer used to prepare the hydrogel-forming material will be at least about 1,000, preferably above about 10,000.

Whatever the nature of the basic polymer components of the hydrogel-forming polymeric gelling agents used in the present compositions, such materials will be crosslinked. Suitable cross-linking agents are well known in the art and include, for example, (1) compounds having at least two polymerizable double bonds; (2) compounds having at least one polymerizable double bond and at least one functional group reactive with the acid-containing monomer material; (3) compounds having at least two functional groups reactive with the acid-containing monomer material; and (4) polyvalent metal compounds which can form ionic cross-linkages.

Cross-linking agents having at least two polymerizable double bonds include (i) di- or polyvinyl compounds such as divinylbenzene and divinyltoluene; (ii) di- or poly-esters of unsaturated mono- or polycarboxylic acids with polyols including, for example, di- or triacrylic acid esters of polyols such as ethylene glycol, trimethylol propane, glycerine, or polyoxyethylene glycols; (iii) bisacrylamides such as N,N-methylenbisacrylamide; (iv) carbamyl esters that can be obtained by reacting polyisocyanates with hydroxyl group-containing monomers; (v) di- or poly-allyl ethers of polyols; (vi) di- or poly-allyl esters of

polycarboxylic acids such as diallyl phthalate, diallyl adipate, and the like; (vii) esters of unsaturated mono- or poly-carboxylic acids with mono-allyl esters of polyols such as acrylic acid ester of polyethylene glycol monoallyl ether; and (viii) di- or tri-allyl amine.

- 5 Cross-linking agents having at least one polymerizable double bond and at least one functional group reactive with the acid-containing monomer material include N-methylol acrylamide, glycidyl acrylate, and the like. Suitable cross-linking agents having at least two functional groups reactive with the acid-containing monomer material include
- 10 glyoxal; polyols such as ethylene glycol; polyamines such as alkylene diamines (e.g., ethylene diamine), polyalkylene polyamines, polyepoxides, di- or polyglycidyl ethers and the like. Suitable polyvalent metal cross-linking agents which can form ionic cross-linkages include
- 15 oxides, hydroxides and weak acid salts (e.g., carbonate, acetate and the like) of alkaline earth metals (e.g., calcium, magnesium) and zinc, including, for example, calcium oxide and zinc diacetate.

- Cross-linking agents of many of the foregoing types are described in greater detail in Masuda et al., U.S. Patent 4,076,663, issued February 28, 1978, incorporated herein by reference. Preferred cross-linking
- 20 agents are the di- or polyesters of unsaturated mono- or polycarboxylic acids with polyols, the bisacrylamides and the di- or tri-allyl amines. Especially preferred cross-linking agents are N,N'-methylenebisacrylamide, trimethylol propane triacrylate and tri-allyl amine.

- 25 The cross-linking agent will generally constitute from about 0.001 mole percent to 5 mole percent of the resulting hydrogel-forming polymeric material. More generally, the cross-linking agent will constitute from about 0.01 mole percent to 3 mole percent of the hydrogel-forming polymeric gelling agent used herein.

- 30 The hydrogel-forming polymer gelling agent herein is at least partially crosslinked, however the degree of crosslinking must be high enough such that the resulting polymer does not exhibit a glass transition temperature (T<sub>g</sub>) below 140°C. Preferably the polymer does not have a T<sub>g</sub> below about 150°C, more preferably not below about 160°C, even
- 35 more preferably has no T<sub>g</sub> below about 180°C, and most preferably does not have a T<sub>g</sub> prior to decomposition of the polymer at temperatures of about 300°C or higher. The T<sub>g</sub> can be determined by differential scanning calorimetry (DSC) conducted at a cooling rate of 20.0 C°/minute

with 5 mg or smaller samples. The T<sub>g</sub> is calculated as the midpoint between the onset and endset of heat flow change corresponding to the glass transition on the DSC heat capacity cooling curve. The use of DSC to determine T<sub>g</sub> is well known in the art, and is described by B. Cassel and M. P. DiVito in "Use of DSC To Obtain Accurate Thermodynamic and Kinetic Data", American Laboratory, January 1994, pp 14-19, and by B. Wunderlich in Thermal Analysis, Academic Press, Inc., 1990.

Slightly crosslinked absorbent polymers, such as the polyacrylate polymers referred to in the skin care industry as "carbomers" in the CTFA Cosmetic Ingredient Dictionary have lower levels of crosslinking than the polymers hereof. Whereas these polymers are effective thickening agents and are commonly used in topical skin compositions to good effect, they would not provide clear compositions containing water insoluble perfumes as obtained according to the present invention.

The hydrogel-forming polymeric gelling hereof are preferably employed in their partially neutralized form. For purposes of this invention, such materials are considered partially neutralized when at least 25 mole percent, and preferably at least 50 mole percent of monomers used to form the polymer are acid group-containing monomers which have been neutralized with a base. Suitable neutralizing bases cations include hydroxides of alkali and alkaline earth metal (e.g. KOH, NaOH), ammonium, substituted ammonium, and amines such as amino alcohols (e.g., 2-amino-2-methyl-1,3-propanediol, diethanolamine, and 2-amino-2-methyl-1-propanol). This percentage of the total monomers utilized which are neutralized acid group-containing monomers is referred to herein as the "degree of neutralization." The degree of neutralization will preferably not exceed 98%.

Hydrogel-forming polymer gelling agent materials can be prepared by reacting monomers and cross-linking agents, as described above, in conventional manners. Prior art hydrogel forming polymeric gelling agent synthesis procedures are well known in the art and are also disclosed in the previously referenced U.S. Pat. Nos. 4,654,039, 4,286,082, and 4,340,706.

Suitable hydrogel forming polymeric gelling agents are commercially available from Hoechst Celanese Corporation, Portsmouth, VA, USA (Sanwet™ Superabsorbent Polymers), Nippon Shokubai, Japan (Aqualic™), and Dow Chemical Company, Midland, MI, USA (Dry Tech™).  
Water Insoluble Perfume

The compositions of the present invention will comprise from about 0.01% to about 5%, by weight of a water-insoluble perfume, preferably from about 0.05% to about 3%, more preferably from about 0.1% to about 1%. By water insoluble perfume, what is meant is that the perfume forms a distinct phase in deionized water at 25°C in the absence of a surfactant or other solubilizer. The perfumes hereof will, in general, either separate to form a distinct phase or form a turbid solution in deionized water, at 25°C, at a concentration of 1.0%, by weight, perfume, wherein such turbid solution has a turbidity of greater than 20 NTU measured as previously described. By perfume, what is meant is a volatile, odoriferous, component of one or more active perfume compounds which exudes a pleasant or otherwise desired aroma at ambient conditions, or which mask odors. The perfume comprises odoriferous, water-insoluble perfume active compounds and may also include additional ingredients, such as diluents, solvents for solid perfume ingredients, and fixatives, etc.

The perfumes hereof are, in general, liquids at ambient temperature and are characterized by a flash point of from about 10°C to about 120°C, more typically from about 25°C to about 95°C (as determined according to ASTM D-56 (c.c.) - Standard Test Method for Flash Point by Tag Closed Tester).

The perfume active compounds are typically incorporated into the perfume components in liquid form, but can also be solids (such as the various camphoraceous perfumes known in the art) which are solubilized in other ingredients of the perfume component.

As discussed, in addition to the perfume active compounds, the perfume hereof can also include additional ingredients such as diluents, solvents for solid perfume ingredients, and fixatives, etc. Diluents may or may not have their own aroma and, to the extent that they do, they are categorized as perfume active compounds. Exemplary diluents and solvents include alcohols (e.g. ethyl alcohol, benzyl alcohol, dipropylene glycol, etc.) and liquid hydrocarbon and hydrocarbon esters (e.g., benzyl benzoate and other hydrocarbons and esters described above). Fixatives are ingredients which prolong the lasting quality of the perfume upon use and can do so by modifying the overall volatility of the perfume component. Some fixatives can function as perfume active compounds, whereas others do not. To the extent that a particular ingredient performs both functions, it shall be considered a perfume active

compound. Exemplary fixatives include musk perfume ingredients described below.

A wide variety of perfume active compounds are described in S. Arctander, *Perfume Flavors and Chemicals*, Vols. I and II., Aurthor, 5 Montclair, NJ, the Merck Index, 8th Edition, Merck & Co., Inc., Rahway, NJ, and Secondini, *Handbook of Perfumes and Flavors*, Chemical Publishing Co., Inc., New York, NY, 1990 (ISBN) 0-8206-0334-1).

The typical perfume will comprise a plurality of individual perfume active compounds, although it can consist essentially of a single perfume 10 ingredient. It is well within the scope of the perfumer of ordinary skill in the art changing ingredients in the perfume component and/or modifying the relative levels of perfume ingredients.

Various types of chemical compounds are commonly known for perfumery uses including: phenolic compounds; essential oils; 15 aldehydes; ketones; polycyclic compounds; esters; and alcohols. Many perfume ingredients contain a combination of functional groups and can be categorized under two or more of the above classes.

From the standpoint of the perfumer, it is convenient to consider the perfume ingredients in terms of the type of aroma it imparts rather 20 than the particular chemical class or classes it may fall within. The perfume components herein can be formulated to provide a variety of odor categories: a non-exclusive list includes woody, sweet, citrus, floral, fruity, animal, spice, green, musk, balsamic, chemical, and mint. A variety of exemplary perfume ingredients are described below for several 25 of the commonly used odor categories, long with their representative (but not necessarily exclusive) chemical categories.

Woody perfume ingredients include cedarwood oil (essential oil), guaicwood oil (essential oil), gamma ionone (ketone), sandalwood oil (essential oil), and methyl cedrylone (ketone).

30 Sweet perfume ingredients include coumarin (ketone), vanillin (4 hydroxy-3methoxy benzaldehyde) (aldehyde), ethyl maltol (Alcohol), phenyl acetaldehyde (aldehyde), heliotropin (aldehyde), acetophenone (ketone), and dihydrocoumarin (ketone).

Citrus perfume ingredients include orange oil (essential oil), lemon 35 oil (essential oil), citral (aldehyde), beta methyl naphthyl ketone (ketone), terpinyl acetate (ester), nonyl aldehyde (aldehyde), terpineol (alcohol), and dihydromyrcenol (alcohol).

Floral perfume ingredients include a variety of floral subcategories, such as rose, lavender, jasmin, and muguet. Rose perfume ingredients include geranyl acetate (ester), geraniol (alcohol), citronellyl acetate (ester), phenyl ethyl alcohol (alcohol), alpha damascone (ketone), beta damascone (ketone), geranium oil (essential oil), and natural rose oil (essential oil). Lavender perfume ingredients include dihydro terpinyl acetate (ester), ethyl hexyl ketone (ketone), lavandin (essential oil), lavender (essential oil), tetra hydro linalool (alcohol), linalool (alcohol), and linalyl acetate (ester). Jasmin perfume ingredients include benzyl acetate (ester), butyl cinnamic aldehyde (aldehyde), methyl benzoate (ester), natural jasmin oil (essential oil), methyl dihydro jasmonate (ester). Muguet perfume ingredients include cycalmen aldehyde (aldehyde), benzyl salicylate (ester), hydroxycitronellol (alcohol), citronellyl oxyacetaldehyde (aldehyde), and hydroxy aldehyde (aldehyde).

Fruity perfume ingredients include ethyl-2-methyl butyrate (ester), allyl cyclohexane propionate (ester), amyl acetate (ester), ethyl acetate (ester), gamma decalactone (ketone), octalactone (ketone), undecalactone (aldehyde), ethyl aceto acetate (ester), benzaldehyde (aldehyde).

Animal perfume ingredients include methyl phenyl acetate (ester), indol (2,3, benzpyrrole) (phenolic), creosol (phenolic), iso butyl quinolin (phenolic), and androstenol (phenolic).

Spice perfume ingredients include anisic aldehyde (aldehyde), anise (essential oil), clove oil (essential oil), eugenol (phenolic), iso eugenol (phenolic), thymol (phenolic), anethol (phenolic), cinnamic alcohol (alcohol), and cinnamic aldehyde (aldehyde).

Green perfume ingredients include beta gamma hexenol (alcohol), brom styrol (alcohol), dimethyl benzyl carbinol (alcohol), methyl heptene carbonate (ester), cis-3-hexenyl acetate (ester), and galbanum oil (essential oil).

Musk perfume ingredients often also function as fixatives. Examples of musk include glaxolide (phenol), cyclopentadecanolide (phenol), musk ketone (ketone), ambrettolide (phenol), tonalid (phenol), and ethylene brassylate (ester).

Balsamic perfume ingredients include fir balsam (essential oil), peru balsam (essential oil), and benzoin resinoid (essential oil).



Chemical perfume ingredients include benzyl alcohol (alcohol), dipropylene glycol (alcohol), ethanol (alcohol), and benzyl benzoate (ester).

Mint perfume ingredients include laevo carvone (ketone), menthol (alcohol), methyl salicylate (ester), peppermint oil (essential oil), spearmint oil (essential oil), eucalyptus (essential oil), anisyl acetate (ester), methyl chavicol (alcohol).

#### Nonionic Surfactant

The compositions of the present invention will comprise from about 0.1% to about 15% by weight, of nonionic surfactant, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%. One or a combination of nonionic surfactants can be used. The amount of nonionic surfactant used must be sufficient to solubilize the perfume thereby enabling clear formulations to be made. "Clear is defined as previously described. Thus, mere emulsions characterized by an opaque or translucent appearance are not included in the present invention. Although in theory the perfume in the present invention is still "emulsified", the droplets of perfume are small enough such that the composition appears to be clear, as would be a "solution" in the theoretical sense. "Solution", for purposes hereof, is defined to include these clear microemulsions.

A wide variety of nonionic surfactants can be used in the present invention. A wide variety of nonionic surfactants can also be used for particular compositions. In general, the level of surfactant used should be above the critical micelle concentration of the composition in order to solubilize the perfume and provide a clear product. The amount of any specific surfactant will depend upon the chemical types of perfume materials used, the level of the perfume, the chemical type and hydrophilic-lipophilic balance (HLB) of the surfactant, the presence of electrolytes in the composition, and other factors as are well known to those skilled in the art. The selection of nonionic surfactant should be made such that the lipophilic portion of the nonionic surfactant is compatible with the perfume and such that the surfactant will form an oil-in-water microemulsion. These surfactants, in general, will have an HLB of from about 6 to about 18, preferably from about 8 to about 15. The average HLB can be calculated as the arithmetic mass average of the individual surfactant components when combinations of nonionic surfactants are used. The average HLB of the entire nonionic surfactant

component is preferably from about 8 to about 15. Methods for determining HLB and the use of HLB as a guide in surfactant selection are described, for example, in Cosmetics Science and Technology, Second Edition, Volume 3, M. S. Balsam and Edward Sagarin, 1974, John Wiley & Sons (New York), pp 583-598, and Colloid and Interface Science, Volume II, Milton Kerker, Academic Press Inc., (New York), 1976, pp 432-435.

As will be understood by those skilled in the art, the optimal nonionic surfactant for use herein will vary according to the particular chemical characteristics of the perfume. In general, it is preferred to use nonionic surfactants having lipophilic portions of chemical types (e.g., ketones, ethers, and the like) that are the same as or similar to the lipophilic ingredients in the water-insoluble perfume.

Nonionic surfactants can broadly encompass compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with a hydrophobic compound, which may be aliphatic or alkyl aromatic in nature as well as other types of nonionic surfactants. Examples of suitable classes of nonionic surfactants are:

1. Alkylphenol ethoxylates e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent may be derived from polymerized propylene, di-isobutylene, octane, or nonane, for example.

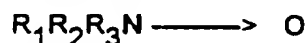
2. Polyoxyethylene surfactants derived from the condensation of ethylene oxide with a hydrophobic group such as an alkyl (e.g., methyl monomeric groups) or polyoxypropylene, or the product resulting from the reaction of propylene oxide and ethylene diamine products. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000 are satisfactory. Also contemplated are polyalkylene oxide block copolymers such as the poly (oxyethylene co-oxypropylene) nonionic surfactants sold under the trad name Pluronics® (BASF Wyandott Corp.) - and the

tradename Emulgin® (Henkel Corporation - Emery Group, Cincinnati, OH USA), such as PPG-2-Cetareth-9 Emulgin®).

Preferred surfactants of this type are propoxylated, ethoxylated ethers of C<sub>12</sub>-C<sub>20</sub> alkyl, preferably C<sub>16</sub>-C<sub>18</sub>, more preferably C<sub>16</sub> alcohols (e.g. cetyl and stearyl alcohols) having an average of from about 2 to about 4 oxypropylene groups, preferably about 2, and from about 7 to about 12 oxyethylene groups, preferably from about 8 to about 10, more preferably about 9.

3. Alcohol ethoxylates - e.g. the condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides such as those corresponding to the following general formula:



wherein R<sub>1</sub> contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R<sub>2</sub> and R<sub>3</sub> contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula represents a semipolar bond). Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyl-di(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di-(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodecoxy-2-hydroxypropyl-di(3-hydroxypropyl) amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula represents a

's dipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethylphosphine oxide, cethylldimethylphosphine oxide, 5 3-dodecoxy-2-hydroxypropyl-di(2-hydroxyethyl) phosphine oxide, stearyl dimethylphosphine oxide, cetyl ethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl) phosphine oxide, dodecyldi(2-hydroxyethyl)- 10 phosphine oxide, tetradecylmethyl-2-hydroxypropyl-phosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually 15 methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl 20 sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

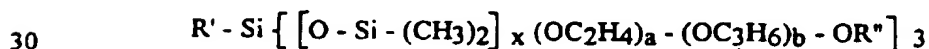
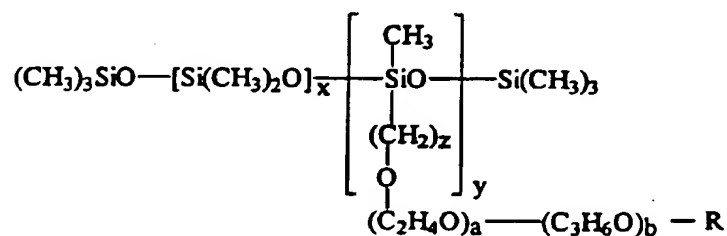
7. Polysorbates, e.g., sucrose esters of fatty acids. Such materials are described in U.S. Patent 3,480,616, e.g., sucrose cocoate 25 (a mixture of sucrose esters of a coconut acid, consisting primarily of monoesters, and sold under the tradenames GRILLOTEN LSE 87K from RITA, and CRODESTA SL-40 from Croda).

8. Alkyl polysaccharide nonionic surfactants are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a 30 hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group. The polysaccharide can contain from about 1.0 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 35 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or

galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units. Optionally there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The alkyl group preferably contains up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkylene moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-  
 5 sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses.  
 10 sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses.

9. Polyethylene glycol (PEG) glyceryl fatty esters, as depicted by the formula  $RC(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$  wherein  $n$  is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and  $RC(O)-$  is an ester wherein  $R$  comprises an aliphatic radical having from about 7 to 19 carbon atoms, preferably from about 9 to 17 carbon atoms, more preferably from about 11 to 17 carbon atoms, most preferably from about 11 to 14 carbon atoms. The combinations of  $n$  from about 20 to about 100, with  $C_{12}$ - $C_{18}$ , preferably  $C_{12}$ - $C_{15}$  fatty esters, for minimized adverse effect on foaming, is preferred.  
 15  
 20

10. Polyalkylene oxide modified dimethylpolysiloxanes, also known as dimethicone copolyols. These materials include the polyalkylene oxide modified dimethylpolysiloxanes of the following formulae:  
 25



wherein  $R$  is hydrogen, an alkyl group having from 1 to about 12 carbon atoms, an alkoxy group having from 1 to about 20 carbon atoms, a

hydroxyl group or C<sub>8</sub> - C<sub>22</sub> triglyceride, R' and R'' are alkyl groups having from 1 to about 12 carbon atoms; x is an integer of from 1 to about 100, preferably from about 20 to 30; y is an integer of 1 to about 20, preferably from 2 to about 10; z is an integer from 1 to 6, preferably from 2 to 4; and a and b are integers of from 0 to about 50, preferably from 20 to 30. Preferred dimethicone copolyols are those of the formula:

Dimethicone copolyols are disclosed in the following patent documents, all incorporated by reference herein: U.S. Patent 4,122,029, Geen et al, issued Oct. 24, 1978; U.S. Patent No. 4,265,878, , issued May 5, 1981; and U.S. Patent No. 4,421,769, Dixon et al., issued Dec. 20, 1983. Commercially available dimethicone copolyols, useful herein, include Silwet Surface Active Copolymers (manufactured by the Union Carbide Corporation); Dow Corning Silicone Surfactants (manufactured by Dow Corning Corporation); Silicone Copolymer F-754 (manufactured by SWS Silicones Corp.) Rhodorsil 70646 Fluid (manufactured by Rhone Poulenc, Inc.); and Fancorsil LIM-1 (dimethicone copolyol eicosinate) from The Fanning Corp. (Chicago, IL, USA).

11. Other surfactants that can be used include the C<sub>10</sub>-C<sub>18</sub>-N-alkyl (C<sub>1</sub>-C<sub>6</sub>) polyhydroxy fatty acid amides. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154 and US Patent 5,194,639, incorporated herein by reference. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub>N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides would be preferred for applications wherein low sudsing is desired.

Preferred surfactants include polyoxyethylene surfactants, polysorbates, alkyl polysaccharide, polyethylene glycol, polyalkylene oxide modified dimethylpolysiloxanes, and mixtures thereof. Especially preferred are mixtures of the dimethicone copolyols and propoxylated ethoxylated ethers of alkyl alcohols, preferably at a weight ratio of from about 0.1:1.0 to about 2.0:1.0, more preferably from about 0.5:1.0 to 1.5:1.0.

Water

The compositions will comprise from about 50% to about 99.75%, by weight, water, preferably from about 65% to about 99.65%, more preferably from about 80% to about 99.55%.

5                   Clear, Thickened Compositions

The compositions of the present invention will have a sufficient amount of hydrogel forming polymeric gelling agent such that the composition has an average viscosity of at least about 4,000 centipoise, at 25°C, as measured using a Brookfield RVT Viscometer equipped with a helipath stand using a 1.435 inch (3.65 cm) T-spindle at 5.0 revolutions/minute, with a plunge rate of 2.3 cm/minute and the measurement taken after a 2.0 minute plunge (i.e., 2.0 minutes after initial contact of the revolving spindle with the top surface of the product), or equivalent. The average viscosity is preferably from about 7000 to about 30,000 centipoise, more preferably from about 7,000 to about 15,000.

The compositions hereof are also clear. As used herein, clear means a turbidity of about 20 NTU or less at 25°C, preferably about 17 NTU or less, more preferably about 15 NTU or less. Turbidity will generally be at least about 5 NTU (25°C), more generally at least about 10 NTU, although lower NTU formulas are not meant to be extended. Turbidity is measured as previously described.

The compositions hereof are essentially free of any carboxylic acid polymers, e.g., polyacrylate or polyacrylic acid-type thickening agents, or other hydrogel-forming polymer having Tg below 140°C, and are preferably free of such polymer having a Tg below about 150°C, more preferably below about 160°C, even more preferably below about 180°C, and most preferably substantially free of such polymer with Tg below 300°C or thermal decomposition of the polymer. By "essentially free" what is meant is any amount that would reduce clarity of the composition to have clarity outside the broadest turbidity limits defined above (20 NTU), and preferably any amount of such polymer that would cause clarity to be outside the preferred turbidity limits defined above.

Optional Ingredients

35                   The present compositions can comprise a wide variety of optional ingredients. However, such optional ingredients should be miscible, soluble, or otherwise solubilizable in the formulations such that the composition remains clear. For example, in the event that such

component is not soluble in water, it may be solubilized by the nonionic surfactant described herein or by another surfactant or solubilizing aid (such as a cosolvent), such that a clear product is provided. Such optional ingredients can be used, for example, for aesthetic purposes, 5 cosmetic purposes, medicinal purposes, skin-protection purposes, or processing ease. Exemplary optional materials are described below. When used, optional ingredients should be present at levels sufficient to provide the intended benefit. In general they will be added at a level of about 0.05%, or higher depending upon the efficacy of the particular 10 ingredient.

#### Conditioning Agents

Conditioning agents suitable for use herein include humectants and emollients. In general, conditioning agents are used at levels of up to about 20%, by weight of the composition, preferably up to about 10%. 15 When added to provide functional benefits, they will generally be added at a level of at least about 0.05%, preferably at least about 0.1%.

Exemplary soluble conditioning agents include C<sub>3</sub>-C<sub>6</sub> diols and triols, e.g., propylene glycol, hexylene glycol, 1,3-dihydroxypropane, butylene glycol, 1,4-dihydroxyhexane, 1,2,6-hexane triol, glycerin, and 20 the like.

Other conditioning agents include: other polyhydroxy alcohols, such as sorbitol; sugars and starches, and derivatives thereof, such as alkoxylated sugars and starches, e.g., alkoxylated glucose; aloe vera; panthenol; hyaluronic acid; lactamide monoethanolamine; octamide 25 monoethanolamine; polyethylene glycol (PEG) and PEG esters of fatty acids and mono-, di-, and tri-glycerides (e.g., PEG-14, PEG-8 caprylate/caprate, PEG-60 almond glyceride) having an average degree of ethoxylation of from about 5 to 200; urea; and guanidine.

Suitable conditioning agents also include soluble emollients such 30 as dimethyl isosorbide, polypropylene glycol ethers of butanediol or other C<sub>4</sub>-C<sub>10</sub> di-hydroxyalkanols having an average total level of propoxylation of about 4 to about 20, preferably from about 8 to about 12 (e.g., PPG-8 butanediol), and polypropylene glycol (PPG)/ polyethylene glycol (PEG) esters of fatty oils, such as oleic, palmitic, stearic and linoleic, having an 35 average degree of propoxylation of about 4 to about 20 and an average degree of ethoxylation of from about 5 to about 200 (e.g. PPG 10-20/PEG 40-100 fatty oils, such as PPG 12/PEG 65 lanolin oil).



Other conditioning agents, including insoluble emollients such as volatile and nonvolatile dimethicone, cyclomethicone dimethiconol, and other silicones, hydrocarbons, fatty esters and alcohols, and the like can also be used as long as the turbidity limitations of the present invention are met.

#### Sensates and Coolants

A wide variety of coolants and sensate materials can be used. Sensates include menthol, acyclic carboxamides such as those described in U.S. Patent 4,230,688, Rowsell et al., issued October 28, 1980, incorporated herein by reference, e.g., N,2,3-trimethyl-2-isopropylbutanamide, and N-substituted-p-menthane-3-carboxamides such as those described in U.S. Patent 4,136,163, Watson et al., issued January 23, 1979, incorporated herein by reference, e.g., N-ethyl-p-menthane-3-carboxamide. Sensates are generally used at levels of from about 0.01%, to about 2%, by weight, preferably from 0.05% to about 1.0%, more preferably from about 0.05% to about 0.5%. Coolants include volatile liquids that evaporate on the skin, thereby resulting with a cooling sensation. Preferred coolants include ethanol, isopropyl alcohol, and witch hazel. The level of such coolants can vary widely. In general, at least about 0.5%, by weight, will be added if used for cooling purposes, preferably at least about 1%. Maximum levels are governed by practical concerns and the degree of cooling sensation desired, as well as the desire to minimize possible stinging, and will generally be no more than about 40%, more generally no more than about 30%.

#### Skin Renewal Agents

Skin renewal agents can also be used in the present compositions, typically at levels of from 0.05% to about 5%, by weight, preferably from about 0.1% to about 2%. These include alpha-hydroxy acids, such as glycolic acid, and glutaric acid, salicylic acid, lactic acid, and other fruit acids.

#### Additional Components

The compositions of the present invention can comprise a wide range of additional components. Examples of these classes of additional components include: anti-acne agents, anti-foaming agents, anti-microbial agents, antioxidants, binders, biological additives, buffering agents, chelating agents, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers, fragrance components, pH adjusters, preservatives, reducing agents,

skin bleaching agents, sunscreen agents (e.g., ultraviolet light absorbers); solvents such as monohydric C<sub>1</sub>-C<sub>4</sub> alcohols (typically at levels from 0% to about 40%, preferably from 0% to about 20%, more preferably from 0% to about 5%), especially ethanol; etc.

- 5 Other nonlimiting examples of these additional components include the following: vitamins and derivatives thereof (e.g., tocopherol, tocopherol acetate, retinoic acid, retinol, retinoids, and the like); polymers for aiding the film-forming properties and substantivity of the composition (such as the copolymer of eicosene and vinyl pyrrolidone, an example of  
10 which is available from GAF Chemical Corporation as Ganex® V-220); preservatives for maintaining the anti-microbial integrity of the compositions; other anti-acne medicaments (e.g., resorcinol, sulfur, salicylic acid, erythromycin, and the like); and skin bleaching (or lightening agents including but not limited to hydroquinone, kojic acid,  
15 antioxidants, chelators and sequestrants.

#### Process for Making

The compositions hereof can be made by mixing the ingredients together according to conventional techniques known in the art.

Preferably, the compositions are made by

- 20 (a) providing a clear aqueous solution comprising from about 0.05% to about 5%, by weight of the composition, of water insoluble perfume, from about 0.1% to about 15%, by total weight, of nonionic surfactant, and from about 10% to about 50%, by weight, water to form a first premix (I);  
25 (b) separately mixing 0.1% to about 10% by weight of the composition, dry polymer weight basis, hydro forming polymeric gelling agent with water to form a clear hydrogel premix II; and  
(c) mixing premix I with premix II;

wherein said composition is clear and has a viscosity of at least about  
30 4,000 centipoise at 25°C.

#### METHOD OF USE

The compositions hereof can be used by topically applying them to the skin, such as via spreading with the hands or an article, or by spraying. In general, from about 0.05 to about 10 g per square  
35 centimeter of skin is applied, preferably from about 0.05 g to about 3 g per square centimeter.

EXAMPLES

Below are examples of the present invention which are provided for purposes of exemplifying specific embodiments of the invention, and are not intended to necessarily limit the invention thereto. The scope of the invention is defined in the claims which follow.

<u>Ingredient (wt. %)</u>		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
10	Water	95.83	93.10	90.08	90.03
	Hydrogel Foaming				
	Polymeric Gelling Agent <sup>1</sup>	0.45	0.40	0.45	0.50
	Glycerin		1.00	2.00	2.00
	PEG/PPG-17/6 Copolymer <sup>2</sup>		2.00	3.00	3.00
15	Perfume	0.50	0.50	0.75	0.75
	Dimethicone Copolyol				
	Eicosanate <sup>3</sup>	1.75	1.75	2.00	2.00
	PPG-2-Cetareth-9 <sup>4</sup>	1.25	1.25	1.50	1.50
	Disodium EDTA	0.02	0.02	0.02	0.02
20	DMDM Hydantoin (and)	0.20	0.20	0.20	0.20
	Iodopropynyl Butylcarbamate <sup>5</sup>				

1 Sanwet IM-1000 (Hoechst Celanese/Fine Chemicals)

2 UCON 75-H-450 (Union Carbide)

3 FANCORSIL LIM-1-1 (Fanning Corp.)

25 4 EMULGIN (Henkel Corp. - Emery Group)

5 Glydant Plus (Lonza, Incorporated)

The above example formulations are made as follows. Seventy to eighty percent of the total required water for the composition is added to a mixing vessel equipped with a rotor-stator homogenizer. The hydrogel forming polymeric gelling agent is added, with mixing at 9500 revolutions per minute (rpm), at a rate of 3 grams/minute. The mixing speed is then increased to 24,000 rpm for five minutes. A clear hydrogel is formed (Premix A). In a separate container equipped with a three blade stirrer, 10-15% of the total required water is added. Mixing is begun at 500 rpm and the disodium EDTA and Glydant Plus™ are added and the preparation is mixed until they are dissolved. Glycerin and PEG/PPG-17% copolymer are then added with mixing at 500 rpm until the solution is clear (Premix B). In another separate mixing vessel equipped with a three blade stirrer, the perfume and dimethicone copolyol eicosanate are mixed at 500 rpm until homogenous. The PPG-2-Cetareth-9 is then added with mixing at 500 rpm until homogenous. The remaining amount

of required water is added slowly (at about 1 gram/minute) with mixing (Premix C). Premix B is added to Premix A at a rate of about 1 gram/minute with stirring via a three blade stirrer, at 500 rpm. Premix C is then added slowly (at about 1 gram/minute) to the mixture of Premixes  
5 A and B with stirring via a three blade stirrer, at 500 rpm. Suitable perfumes include, for example, those utilized in Old Spice™ (Procter & Gamble) skin care products, and equivalents. The final product is a fragrant, thickened, clear hydrogel skin conditioning composition.

What is Claimed is:

1. A clear, thickened, fragrant topical skin care composition characterized in that it comprises:

- (a) from 0.1% to 10%, by weight, hydrogel forming polymeric gelling agent, calculated on a dry polymer weight basis;
- (b) from 0.05% to 5%, by weight, water-insoluble perfume;
- (c) from 0.1% to 15%, by weight, nonionic surfactant; and
- (d) from 50% to 99.75%, by weight, water;

wherein said composition is clear and has a viscosity at 25°C of at least 4,000 centipoise.

2. A skin care composition as in Claim 1, wherein said hydrogel forming polymeric gelling agent is selected from the group consisting of polyacrylic acid polymer, polymethacrylic acid polymer, polyacrylic acid/polymethacrylic acid copolymer and polymers derived from anhydride salts of acrylic acid, salts of methacrylic acid, and mixtures thereof.

3. A skin care composition as in Claim 1 or 2, wherein said hydrogel forming polymeric gelling agent does not have a  $T_g$  below 180°C, and preferably does not have a  $T_g$  prior to decomposition at temperature of about 300°C or higher.

4. A skin care composition as in Claim 1, 2, or 3, wherein said composition has a turbidity of 17 NTU or less, preferably 15 NTU or less.

5. A skin care composition as in Claim 1, 2, 3, or 4, wherein said nonionic surfactant is selected from the group consisting of dimethicone copolyols, propoxylated ethoxylated ethers of alkyl alcohols, and mixtures thereof.

6. A skin care composition as in Claim 5, wherein the ratio of said dimethicone copolyol to said propoxylated ethoxylated ether of alkyl alcohol is from 0.1:1.0 to 2.0:1.0, preferably from 0.5:1.0 to 1.5:1.0.

7. A skin care composition as in Claim 1, 2, 3, 4, 5, or 6, wherein said composition comprises from 0.2% to 5% of said hydrogel forming polymeric gelling agent, from 0.05% to 3% of said perfume, and from 0.1% to 10% of said nonionic surfactant.

8. A skin care composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said composition has a viscosity of from 7,000 to 30,000 centipoise at 25° C, and preferably comprises 0.3% to 9%, by weight, of said hydrogel forming polymeric gelling agent.

9. A skin care composition as in Claim 1, 2, 3, 4, 5, 6, 7, or 8, further comprising a skin conditioning agent, coolant, sensate, skin renewal agent, or a combination thereof.

10. A skin care composition as in Claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, further comprising a skin conditioning agent selected from the group consisting of polyethylene glycol, polyethylene glycol esters of fatty acids and mono-, di-, and tri- glycerides, polypropylene glycol ethers of C4-C10 di-hydroxyalkanols, polypropylene glycol/polyethylene glycol ethers of fatty oils, and combinations thereof.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/11311

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/48 A61K7/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 21234 (COLLABORATIVE LABORATORIES) 29 September 1994 see the whole document ---	1,2,7
X	US,A,5 034 220 (HELIOFF ET AL.) 23 July 1991 see the whole document ---	1,2,5-7
A	EP,A,0 261 351 (ROURE BERTRAND DUPONT SOCIÉTÉ ANONYME) 30 March 1988 see the whole document ---	1-10
P,A	US,A,5 409 630 (LYEY ET AL.) 25 April 1995 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 January 1996

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 95/11311

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9421234	29-09-94	US-A- 5437867	01-08-95
US-A-5034220	23-07-91	AU-B- 7851191	07-01-92
		EP-A- 0581764	09-02-94
		WO-A- 9119477	26-12-91
EP-A-261351	30-03-88	JP-A- 1052470	28-02-89
US-A-5409630	25-04-95	AU-B- 1693295	21-08-95
		WO-A- 9521239	10-08-95